



Occurrence of perfluoroalkyl substances in selected Victorian rivers and estuaries: An historical snapshot



Mayumi Allinson^a, Nobuyoshi Yamashita^b, Sachi Taniyasu^b, Eriko Yamazaki^b,
Graeme Allinson^{c,*}

^a Department of Chemical Engineering, The University of Melbourne, Parkville, Victoria, 3010, Australia

^b National Institute of Advanced Industrial Science and Technology (AIST), 16-1 Onogawa, Tsukuba, Ibaraki, 305-8569, Japan

^c School of Science, RMIT University, Melbourne, Victoria, 3001, Australia

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ABSTRACT

This reconnaissance study was undertaken in 2012 to examine the occurrence of common perfluoroalkyl substances (PFAS), including perfluoroalkyl sulphonic acids and perfluoroalkyl carboxylic acids in rivers and estuaries in Port Philip Bay, Victoria, Australia. In total, 19 PFAS were screened in grab samples of water using a combination of solid phase extraction and liquid chromatography - mass spectrometry measurement techniques. Eighteen of the PFAS screened were observed in samples. The highest level of PFOS observed at a freshwater site was 0.045 µg/L; this concentration is approximately half the draft Australian 95% species protection level for total PFOS. The highest level of PFOA in the study (0.014 µg/L) was some four orders of magnitude lower than the draft Australian trigger value for PFOA (220 µg/L). However, none of the PFAS observed at the freshwater sites had research quotient (RQ) or toxicity unit (TU) values above 1 or -3, respectively. The highest concentration of PFOS observed at an estuarine site was 0.075 µg/L; the highest level of PFOA, 0.09 µg/L). There are no Australian marine water quality trigger values for PFAS, so potential risk was assessed using the European environment quality standards (EQS) adopted in EU Directive 2013/39/EU, RQ and TU methods. In that context, none of the PFAS observed at estuary sites had concentrations higher than the EU standards, or RQ above 1 or Log₁₀TU above -3. Together these assessments suggest none of the PFAS screened would have posed an acute risk to organisms in the fresh or estuary waters studied at the time of sampling on an individual or collective basis. However, the detection of these PFAS in Victorian estuaries highlights that the issue is not just an issue for more densely populated countries in the northern hemisphere, but also potentially of concern in Australia. And, in that context, more sampling campaigns in Port Philip Bay are of paramount importance to assess the potential risk posed by these compounds to aquatic ecosystems.

1. Introduction

Perfluoroalkyl substances (PFAS), such as PFOS (perfluorooctanesulfonic acid) and PFOA (perfluorooctanoic acid) and related shorter and longer chain analogues, are ubiquitous contaminants of soils, water and biota (Wang et al., 2017). Such chemicals were, and are still, designed to be chemically and biologically stable in the products into which they were/are applied and so they are persistent in the environment. They have been frequently found in terrestrial and marine wildlife and also human blood. Acute toxicity data for many of these compounds are limited compared to that available for other persistent organic chemicals (Wang et al., 2017), with mortality not observed until

organisms are exposed to moderate to high (mg/L) concentrations (Giesy et al., 2010). Laboratory animal experiments have, however, suggested that potential developmental, reproductive, and other systematic effects are observed at high µg/L concentrations, and that long chain PFAS are bio-accumulative and potentially carcinogenic (as reviewed in DeWitt et al., 2015; Wang et al., 2017).

In Australia much of the recent concern around PFAS has been driven by the recognition that the PFAS in aqueous film forming foams (AFFFs) used for emergency response and regular training exercises at military and civilian airports and training bases has resulted in contamination of local soils and groundwaters (Baduel et al., 2017), with some recognition of the potential for contaminated landfill leachate to contaminate aquatic

* Corresponding author.

E-mail address: graeme.allinson@rmit.edu.au (G. Allinson).

ecosystems (Gallen et al., 2017). There have been reports of groundwater contamination in all Australian states and territories, with perhaps the most publicised cases contamination of drinking water bores in Katherine, 270 km southeast of Darwin in the Northern Territory, and around the RAAF Williamtown airbase, 170 km north east of Sydney in New South Wales. In Victoria, the Environment Protection Authority has notified the public of elevated PFAS levels near Department of Defence locations in East Sale, Wodonga and Hastings, and fire training facilities in Fiskville, Penshurst, Bangholme, Wangaratta, Huntly, Fulham and Longerenong, all as a result of chemicals used in firefighting foam (Australian Water Association, 2017).

While there is now a reasonable understanding of the ubiquitous nature of PFAS contamination of water and biota internationally, at the time of this study (2012) there were no published data on PFAS in natural, surface waters in Victoria, Australia. This reconnaissance survey, therefore, sought to obtain a snapshot of the occurrence and concentrations of common PFAS in surface water samples collected from seven creeks and estuaries in Port Philip Bay catchment, Victoria, and to assess the risk to aquatic organisms therein by comparing observed concentrations with regulatory guideline values.

2. Materials and methods

2.1. Study sites

Seven sites in and around Melbourne were chosen for this study (Fig. 1; A-G). The sites were selected because they were part of other ongoing ecological investigations of river health. A single 'grab' or spot sample of water (1 L) was collected from each of the seven sites on a single occasion during September 2012.

Sites A (estuary) and G (freshwater) were on the Werribee River. Approximately 25% of the Werribee River catchment is forested, with ~66% of the total catchment area used for grazing. The remaining 10% of the catchment is urbanised. At the time of this study there were two small sewage treatment plants (STPs) in the upper Werribee River catchment licensed to discharge to the river (<~5 000 m³ annual discharge). Site B (estuarine) was on Laverton Creek a few hundred

metres from its discharge into PPB. The entire length of this creek is within the western suburbs of Melbourne, including through heavily industrialized areas. Site C (estuary) was on Kororoit Creek. This long stream is ~50 km long flows almost entirely through the suburbs of north western Melbourne, including several industrialised areas before emptying into Altona Bay; there are no known STPs discharging into either Laverton or Kororoit creek upstream of sampling sites. Site D (estuary) was in the Yarra River estuary. This river is ~240 km long, and originates in the Yarra Ranges east of Melbourne and several small STPs discharged treated effluent into the upper Yarra River (<~5000 m³ total annual flow) in 2012. Site E (freshwater) was on Stony Creek in the western suburbs of Melbourne downstream of an industrialised area. As far as the Authors know, there are no STP discharges into this creek. Site F (estuary) was at the end of the Maribyrnong River prior to its confluence with the Yarra River. Most (~80%) of the Maribyrnong River is used for agriculture, principally grazing and horticulture, with only ~10% of the catchment urbanised. In 2012 there were two small STPs in the upper catchment discharging to the river (<~3000 m³ annual discharge).

2.2. Sample preparation and chemical analysis

In total, 19 PFAS were screened including the sulphonates PFHxS and PFOS, and the carboxylates PFHxA and PFOA (Table 1). Detailed analytical procedures are reported in Taniyasu et al. (2008) but, in short, samples were extracted with Oasis® WAX cartridges (150 mg, 6 mL, 30 µm, Waters) and eluted with 0.1% NH₄OH in methanol. The concentrations of PFAS in the extracts were determined using high-performance liquid chromatography coupled with tandem mass spectrometry (HPLC-MS/MS). In short, an HP1100 HPLC-system (Agilent Technologies, Palo Alto, CA) was equipped either with a Betasil C18 column (2.1 mm i.d. 50 mm in length, 5 µm; Thermo Hypersil-Keystone, Bellefonte, PA), with a XDB-C8 (12.5 mm 2.1 mm, 5 µm; Agilent Technologies, Foster City, CA) as a guard column (for perfluorosulphonates analysis), or a RSpak JJ-50 2D column (2.0 mm i.d. 150 mm in length, 5 µm; Shodex, Showa Denko K.K., Kawasaki, Japan) with an OPTI-GUARD 1mm DVB guard column (Optimize Technologies, OR, USA) (for perfluorocarboxylates analysis). A triple-quadrupole mass spectrometer,

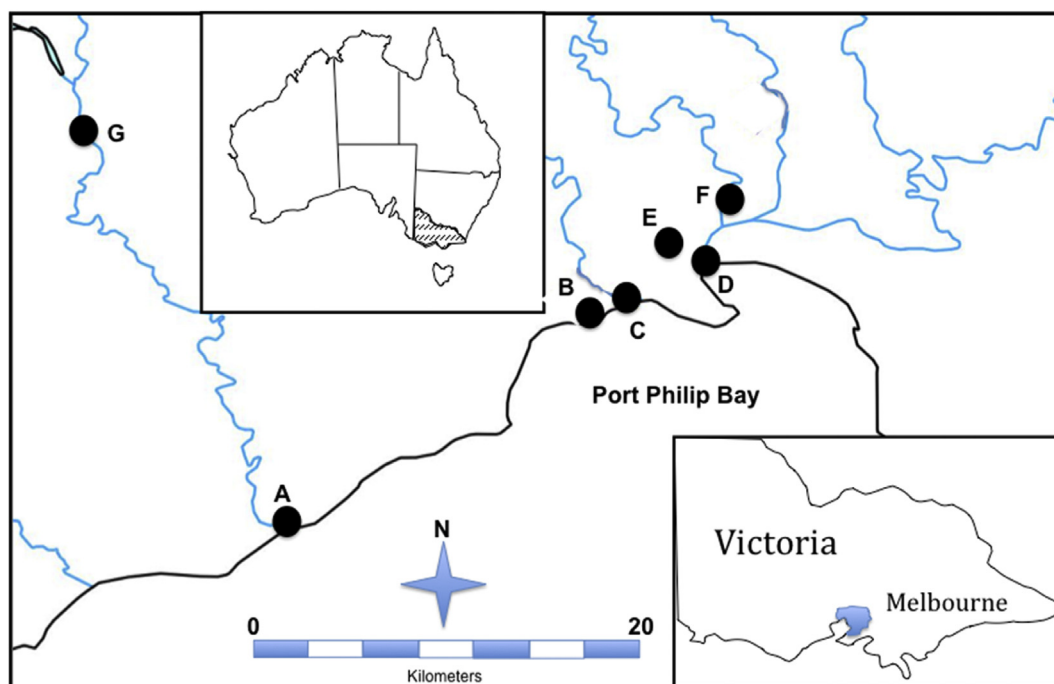


Fig. 1. Approximate location of sampling sites in and around the city of Melbourne (M) in Victoria, Australia.

Table 1
Summary of PFAS detected in water samples.

Chemical	Site						
	Estuarine sites					Freshwater sites	
	A	B	C	D	F	E	G
Sulfonates	(ng/L)					(ng/L)	
PFBS	0.8	7.0	6.7	0.4	0.8	2.6	0.5
PFHxS	4.2	42.3	29.6	3.0	7.0	15.4	2.9
PFOS	3.9	74.9	74.1	5.1	13.9	45.2	6.5
PFDS		0.0	0.1	0.0	0.1	0.1	0.0
FOSA	0.0	0.1	0.3	0.0	0.1	1.0	0.0
N-EtFOSA							
N-EtFOSAA	0.2	0.3	0.8	0.2	1.5	1.9	0.1
Carboxylates							
PFBA	2.9	10.2	11.1	1.7	2.8	8.8	2.7
PFPeA	3.1	9.7	6.4	1.2	2.1	9.7	3.5
PFHxA	2.1	22.6	10.9	1.5	2.1	11.4	2.4
PFHpA	1.8	8.9	6.9	1.2	1.5	6.0	1.8
PFOA	2.2	9.2	8.5	1.7	2.2	14.5	1.2
PFNA	0.2	1.2	6.4	0.4	3.3	2.2	0.1
PFDA	0.2	0.5	1.7	0.4	1.2	4.2	0.7
PFUnDA	0.1	0.2	1.1	0.2	0.7	0.5	0.2
PFDoDA	0.0	0.1	0.3	0.2	1.1	0.9	0.1
PFTeDA			0.0	0.0	0.1	0.1	0.0
PFHxDA	0.0	0.0	0.1		0.1	0.1	
PFocDA					0.0	0.0	

No value, <LOR.

Table 2a
Summary of selected (most commonly reported) PFSA concentrations reported in rivers in Australia and internationally (ng/L).

Country	PFBS	PFHxS	PFOS	PFDS	FOSA	Reference
Australia	0.5–2.6	2.9–15	6.5–45	0.0–0.1	0.0–1.0	This study
Australia		n.d. - 2.5	n.d. - 4.9			Gallen et al. (2014)
Canada	n.d. - 14	n.d. - 180	n.d. - 190			D'Agostino and Mabury (2017)
China	n.d. - 6.7		2.7–41			Zhao et al. (2016)
China	0.0–14	n.d. - 1.4	n.d. - 9.7		n.d. - 2.5	Lu et al. (2015)
China	n.d. - 31		0.3–290		n.d. - 0.2	Pan et al. (2014a)
China	n.d. - 42	n.d. - 4.5		n.d. - 0.2	n.d. - 0.6	Pan et al. (2014b)
China			n.d. - 8.4			Yao et al. (2014)
China	0.16 - 1.01	0.01–0.43	0.01–1.57			Loi et al. (2013)
China			n.d. - 2.25			Ju et al. (2008)
France	n.d. - 3.1	0.3–7.8	0.3–16	n.d. - 0.1	n.d. - 0.2	Munoz et al. (2018)
France			n.d. - 6			Bach et al. (2017)
France			n.d. - 173	n.d. - 0.21	n.d. - 0.73	Boiteux et al. (2017)
France	n.d. - 29	n.d. - 217	n.d. - 4.6			Munoz et al. (2015)
Germany		n.d. - 5.6	0.89–10.1			Llorca et al. (2012)
Germany	0.22–118	n.d. - 14.5				Möller et al. (2010)
Germany	n.d. - 3.7	n.d. - 0.5	0.2–2.9			Ahrens et al. (2009)
India	n.d. - 10	n.d. - 0.3	n.d. - 1.7	n.d. - 0.1	n.d. - 0.1	Sharma et al. (2016)
Italy		n.d. - 5	n.d. 43			Castiglioni et al. (2015)
Italy	n.d. - 1670	n.d. - 36	n.d. - 150			Valsecchi et al. (2015)
Italy			n.d. - 25			Loos et al. (2008)
Japan	0.1–2.0	n.d. - 6.8	0.5–8.0	n.d. - 0.1		Ye et al. (2014)
Japan		n.d. - 22	n.d. - 99		n.d. - 4.0	Zushi et al. (2011)
Japan			n.d. - 4.6			Takagi et al. (2008)
Korea		n.d. - 4.0	n.d. - 15			Lam et al. (2014)
Korea	n.d. - 2.3	n.d. - 6.5	n.d. - 33	n.d. - 0.3		Lam et al. (2016)
Malta		n.d. - 2.5	n.d. - 8.6			Sammut et al. (2017)
Norway		n.d. - 0.4	n.d. - 0.7			Kwok et al. (2013)
Singapore	1.4–55	0.4–16	1.5–24		n.d. - 6.1	Chen et al. (2017)
Singapore		1.2–68	1.3–156		n.d. - 3.15	Nguyen et al. (2011)
South Africa	n.d. - 25	n.d. - 7.6	0.4–36			Groffen et al. (2018)
Spain		12–37	0.01–128			Campo et al. (2016)
Spain	0.4–4.1	14–33		0.0–271000		Campo et al. (2015)
Spain			20–348			Flores et al. (2013)
Spain		n.d. - 37	n.d. - 2700			Llorca et al. (2012)
Sweden	0.0–19	0.1–18	0.0–6.9		0.0–0.5	Nguyen et al. (2017)
Switzerland	0.4 - 20	5.8–20	29–82			Huset et al. (2008)
USA			n.d. - 24			Newsted et al. (2017)
USA	n.d. - 84	n.d. - 371	n.d. - 296			Nakayama et al. (2010)
USA		n.d. - 4.05	n.d. 9.3	n.d. - 0.34	n.d. - 0.47	Kim and Kannan (2007)
USA			16.8–144			Hansen et al. (2002)
Vietnam	n.d. - 5.3	n.d. - 6.6				Duong et al. (2015)
Vietnam	n.d. - 8.3	n.d. - 6.0	n.d. - 40			Lam et al. (2017)

supplied by Micromass (Quattro Ultima Pt, Beverly, MA), used an electrospray ionization (ESI) interface in negative ionization mode. The flow rate was set to 300 $\mu\text{L}/\text{min}$ and 10 μL of the sample was injected. Limits of Quantitation (LOQ) varied depending on the chemical and column/instrument conditions used, but ranged from 0.02 to 0.50 ng L^{-1} . For full details of the instrumental conditions and quantification for PFAS analysis, readers are directed to Taniyasu et al. (2008).

2.3. Data analysis and risk methodology

Data has been truncated to report only positive detects relevant to exceedances of regulatory guidelines or ecotoxicological benchmarks. Observed concentrations were first compared with the ANZECC and ARMCANZ (2000) water quality guidelines trigger values for water discharged to receiving freshwater and marine aquatic environments. Where no local guideline values were available, concentrations were compared to European environment quality standards (EQS) adopted in EU Directive 2013/39/EU. Thereafter two additional methods were used to evaluate the potential risk to aquatic organisms and ecosystems: the risk quotient (RQ) and toxicity unit (TU) methods. For the RQ we followed the process outlined by Thomatou et al. (2013) to generate general case (RQ_{median}) and the worst case (RQ_{max}) scenarios. Long-term ecotoxicological effects data were extracted from the U.S. Environmental Protection Agency (2019). In the first instance, data for the rainbow trout (*Oncorhynchus mykiss*) was used for the calculation of the PNECs; where

this data was not available any alternative data for a fish was used. Similar processes were used for aquatic invertebrates, plants and algae. Short term EC50 (lethal/effect) data were obtained from the database when long-term data were not available. The PNEC values were calculated by dividing the lowest effect concentration of the most sensitive species by 10 where chronic data was available from all four trophic levels, 50 where long-term data was available from three trophic levels or at least one effect level used was an acute value, and 100 for all other cases. We calculated the toxic unit (Log_{10}TU) for each PFAS according to the method of Liess and Von Der Ohe (2005) by dividing the observed water concentration by a measure of the toxicity (as used for measuring RQ). The toxic units for the PFCAs and PFSAs screened were considered individually and on a group basis for both freshwater and estuarine sites.

3. Results and discussion

3.1. PFAS concentrations at freshwater sites E and G

The main aim of this reconnaissance survey was to obtain a snapshot of the occurrence of 19 common PFAS in five urban/peri-urban estuaries, one urban freshwater stream and one rural river. In that context, water samples collected from the urban freshwater site E were more highly contaminated than the rural freshwater site G (site E, ΣPFAS 125 ng/L cf. site G, 23 ng/L). Moreover, site E was more contaminated with PFOS than

the rural freshwater site G (site E, 45 ng/L cf. site G, 6.5 ng/L, respectively; Table 1)). There were, and still are, no published studies of perfluoroalkylsulphonic acid (PFSA) concentrations in Victorian freshwaters with which to compare our data. However, PFSA concentrations observed at site G in this study were consistent with levels in Queensland (Gallen et al., 2014). Specifically, the levels of PFOS at site G (6.5 ng/L) are consistent with levels reported in the freshwater sections of the Brisbane River (up to 4.9, respectively; Gallen et al., 2014)). The PFSA concentrations at site E were, however, an order of magnitude higher than reported in the Brisbane River (Gallen et al., 2014), except for PFBS, which was higher in a tributary. Overall, our freshwater site data is consistent with reports of PFSA concentrations in rivers in China (e.g. Zhao et al., 2016), Germany (e.g. Möller et al., 2010), Japan (Ye et al., 2014), Korea (Lam et al., 2016), Norway (Kwok et al., 2013), and the USA (Newsted et al., 2017) (see Table 2a).

Perfluoroalkylcarboxylic acid (PFCA) chemical concentrations were also higher at site E than at site G (e.g. PFOA 14.5 ng/L cf. 1.2 ng/L; Table 1). Again, there were, and still are, no published studies of PFCA concentrations in Victorian freshwaters with which to compare our data, although PFCA concentrations observed at site G in this study were consistent with levels in Queensland (Gallen et al., 2014). For example, the levels of PFOA levels at site G (1.2 ng/L) are consistent with levels reported in the freshwater sections of the Brisbane River (up to 1.4 ng/L; Gallen et al., 2014)). The PFCA concentrations at site E were, however, an order of magnitude higher than reported in the Brisbane River (Gallen

Table 2b

Summary of selected (most commonly reported) PFCA concentrations reported in rivers in Australia and internationally (ng/L).

Country	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	Reference
Australia	2.6–8.8	3.5–9.7	2.4–11	1.8–6.0	1.1–14	0.1–2.2	0.7–4.2	This study
Australia			0.12–1.1	n.d. - 0.5	0.3–1.4		n.d. - 0.1	Gallen et al. (2014)
Canada		n.d. - 190	n.d. - 120	n.d. - 60	n.d. - 59			D'Agostino and Mabury (2017)
China	6.4–54		8.0–47	n.d. - 3.8	2.0–42	0.8–25	0.2–101	Zhao et al. (2016)
China	n.d. - 5	n.d. - 3.5	0.1–41	n.d. - 4.3	0.3–200	n.d. - 2.9	n.d. - 2.6	Lu et al. (2015)
China	0.2–2.5	0.2–4.6	n.d. - 4.6	n.d. - 6.2	0.2–22	0.2–2.0	0.2–1.4	Pan et al. (2014a)
China	0.4–8.4	n.d. - 2.6	0.1–23	n.d. - 2.6	0.5–18	n.d. - 0.9	n.d. - 0.3	Pan et al. (2014b)
China					6.4–2.6			Yao et al. (2014)
China			0.15–1.18		0.31–2.48	0.04–0.56	0.01–0.39	Loi et al. (2013)
China					0.17–36			Ju et al. (2008)
France		0.1–6.4	0.2–7.7	0.1–2.8	0.2–5.9	n.d. - 2.0	n.d. - 1.5	Munoz et al. (2018)
France			n.d. - 188					Bach et al. (2017)
France	n.d. - 4	n.d. - 4	n.d. - 8	n.d. - 7	n.d. - 13			Boiteux et al. (2017)
France	n.d. - 11	n.d. - 35	n.d. - 86	n.d. - 16	n.d. - 36	n.d. - 30	n.d. - 10	Munoz et al. (2015)
Germany	n.d. - 23	n.d. - 9.4	n.d. - 13	n.d. - 24	n.d. - 6.5			Llorca et al. (2012)
Germany	n.d. - 188	n.d. - 27.6	n.d. - 13.8	n.d. - 1.31	0.61–17.9			Möller et al. (2010)
Germany		0.7–2.8	1.6–5.0	0.8–2.4	2.6–9.7	0.2–0.9	n.d. - 0.7	Ahrens et al. (2009)
India	n.d. - 1.0	n.d. - 3.0	0.4–4.7	0.3–3.3	0.1–1.2	n.d. - 0.2	n.d. - 0.2	Sharma et al. (2016)
Italy	n.d. - 52	n.d. - 41	n.d. - 62	n.d. - 93	3–303	n.d. - 174	n.d. - 99	Castiglioni et al. (2015)
Italy	n.d. - 401	n.d. - 505	n.d. - 346	n.d. - 946	n.d. - 6480	n.d. - 70	n.d. - 51	Valsecchi et al. (2015)
Italy				n.d. - 18	1–1270	n.d. - 13		Loos et al. (2008)
Japan					n.d. - 92			Takagi et al. (2008)
Japan	n.d. - 1.4	0.5–2.4	0.3–5.0	0.2–2.2	0.6–5.7	0.3–5.0	n.d. 0.2	Ye et al. (2014)
Japan			n.d. - 423	n.d. - 460	n.d. - 3703	n.d. - 1120	n.d. - 122	Zushi et al. (2011)
Korea			n.d. - 7.9	n.d. - 3.4	n.d. - 8.3	n.d. - 4.4	n.d. - 4.8	Lam et al. (2014)
Korea			n.d. - 9.0	n.d. - 7.2	n.d. - 42	n.d. - 7.6	n.d. - 7.0	Lam et al. (2016)
Malta			n.d. - 17	n.d. - 11	n.d. - 16	n.d. - 2.5	n.d. - 4.4	Sammut et al. (2017)
Norway	0.5–1.8	n.d. - 2.4	0.2–0.3	0.1–0.2	0.1–0.4	<0.1	<0.1	Kwok et al. (2013)
Singapore	1.0–22	0.5–19	0.4–7.1	1.1–14	2.0–21	1.2–530	1.2–8.6	Chen et al. (2017)
Singapore				n.d. - 14.4	5.4–38	0.9–78	0.7–28	Nguyen et al. (2011)
South Africa		5.7–45	n.d. - 20	n.d. - 2.5	0.6–4.6	n.d. - 1.8		Groffen et al. (2018)
Spain	5.2–644	0.1–2.8	1.4–18	0.6–20	0.1–52	0.9–20	0.1–213	Campo et al. (2016)
Spain	0.1–111	0.1–2.5	0.6–25	0.6–31	0.1–146	0.8–52	0.1–4.3	Campo et al. (2015)
Spain					4.9–44			Flores et al. (2013)
Spain	n.d. - 125	n.d. - 13	n.d. - 31	n.d. - 27	n.d. - 68	n.d. - 52	n.d. - 213	Llorca et al. (2012)
Sweden	0.5–3.7		0.5–4.2	0.4–1.7	0.2–4.2	0.1–5.8	0.0–4.4	Nguyen et al. (2017)
Switzerland				n.d. - 8.7	3.6. - 11			Huset et al. (2008)
USA	n.d. - 19				n.d. - 6.1			Newsted et al. (2017)
USA	n.d. - 458	n.d. - 45	n.d. - 140	n.d. - 90	n.d. - 125	n.d. - 73	n.d. - 42	Nakayama et al. (2010)
USA				1.15–12.7	3.27–15.8	n.d. - 3.51	0.25–3.58	Kim and Kannan (2007)
USA					n.d. - 598			Hansen et al. (2002)
Vietnam		n.d. - 5.8	n.d. - 5.6	n.d. - 9.2	n.d. - 18	n.d. - 0.9	n.d. - 1.3	Duong et al. (2015)
Vietnam			n.d. - 4.3	n.d. - 7.8	n.d. - 54	n.d. - 4.8	n.d. - 1.4	Lam et al. (2017)

et al., 2014), again with the exception of a higher PFBS level observed in a tributary. Site E is downstream of an industrial park, perhaps suggesting a point source for PFAS in that catchment. Overall, however, our freshwater site data is consistent with reports of PFCAs concentrations in rivers in China (e.g. Pan et al., 2014a,b), France (e.g. Munoz et al., 2018), Korea (Lam et al., 2014), Switzerland (Huset et al., 2008), and Vietnam (Duong et al., 2015) (see Table 2b).

3.2. PFAS concentrations at estuary sites A, B, C, D and F

Water samples collected from estuary sites B and C (ΣPFAS 187 and 165 ng/L, respectively) were much more highly contaminated than sites A, D and F (ΣPFAS 22, 17 and 42 ng/L, respectively). And, in that context, estuaries B and C were also the most highly contaminated with PFOS (75 ng/L and 74 ng/L, respectively; Table 1) and PFHxS (42 ng/L and 30 ng/L, respectively). These two sites are downstream of some of the most heavily industrialised areas of Melbourne and both also had significant levels of PFOA (site B, 9 ng/L; site C, 9 ng/L), PFHxA (site B, 23 ng/L; site C, 11 ng/L), and PFBA (site B, 10 ng/L; site C, 11 ng/L). There are fewer studies of PFAS in estuaries with which to compare our data than those reported for freshwaters, although the PFAS concentrations observed in our estuaries are consistent with levels reported elsewhere in Australia. For example, the levels of PFOS and PFOA concentrations (up to 74 and 9.1 ng/L) are consistent with levels reported in the estuarine sections of the Brisbane River (up to 34 and 11 ng/L, respectively; Gallen et al.,

2014) and Sydney harbour (up to 21 and 6.4 ng/L, respectively; Thompson et al., 2011). Overall, our estuary data is consistent with reports of PFAS concentrations in estuaries in China (e.g. Shao et al., 2016; Wang et al., 2011), Japan (Ahrens et al., 2010), Korea (Lam et al., 2016; Hong et al., 2013), and the USA (Konwick et al., 2008) (see Table 3).

Simcik and Dorweiler (2005) proposed that a PFHpA/PFOA ratio greater than one is indicative of atmospheric PFAS sources, but of non-atmospheric sources associated with urban areas when lower than one. In that context, only Site G had a ratio >1 (1.55), suggesting long distance atmospheric transport as the source of much of the PFAS entering the upper reaches of the Werribee River. All other sites had a PFHpA/PFOA ratio less than one, with Site E ratio 0.4, further suggesting a point source of PFAS on Stony Creek above that sampling point.

3.3. PFAS loads entering Port Philip Bay

To estimate the amount of PFAS entering Port Philip Bay the PFAS concentration at the Yarra and Werribee River outlet sites was multiplied by river flow in 2012–13 (no flow data could be obtained for Laverton Creek or Kororoit Creek for the period in question; the Maribyrnong River enters the Yarra River upstream of the Yarra River site and so contributes to the flux observed at Site D). The estimated yearly PFAS input to PPB is, however, subject to uncertainties due to the possible variations in PFAS concentrations in the river throughout the year, which was not covered in our sampling, resulting from both changes in inputs

Table 3
Summary of selected (most commonly reported) PFAS concentrations reported in estuaries and embayments.

Country	Chemical											Reference
	PFBS	PFHxS	PFOS	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnDA	
	(ng/L)											
Australia	0.4–7.0 0.6–2.6	3.0–30 0.1–17	3.9–74 0.3–34	1.7–11	1.1–9.7	1.5–22 0.4–6.2	1.2–8.9 0.2–3.7	2.1–9.1 0.1–11	0.2–6.4 0.2–1.3	0.2–1.7 0.1–1.2	0.0–1.1	This study Gallen et al. (2014)
	152 +/- 24		323 +/- 25			231 +/- 17	253 +/- 40	225 +/- 33	303 +/- 36	334 +/- 53		Kaserzon et al. (2012)
	1.2–1.5	2.7–4.3	7.5–21			2.8–3.2	1.4–2.0	4.2–6.4	0.6–2.0	0.8–1.6	0.2–0.3	Thompson et al. (2011)
China	2.3–9.6	n.d. - 0.6	n.d. - 0.8	25–105	20–79	4–11	0.8–2.3	9–16	0.4–0.8	n.d. - 0.3		Shao et al. (2016)
			2.38	107	142	289	211	13666	1.75			Heydebreck et al. (2015)
			n.d. - 30.9					2.58–81.7				Wang et al. (2011)
			n.d. - 2.25 n.d. - 99					0.17–37 n.d. - 260				Ju et al. (2008) So et al. (2007)
Germany		0.37–1.65	n.d. - 1.62	n.d. - 3.11	0.81–3.83	1.31–4.38	n.d. - 7.74	1.57–11.56	0.12–2.25	n.d. - 2.12	n.d. - 0.34	Heydebreck et al. (2015)
Japan		0.5–1.0	0.9–2.2	8–20	2–4	0.5–1.5	0.4–1.5	2.5–9.0	2–5			Ahrens et al. (2010)*
			0.78–17					2.7–63				Sakurai et al. (2010)
		0.02–56	0.34–57					1.8–192	0.16–71			Yamashita et al. (2005)
		3.3–5.6	12.7–25.4					154–192				Yamashita et al. (2004)
			0.5–25.2									Saito et al. (2003)
Korea	n.d. - 0.4	n.d. - 1.1	n.d. - 4.2			n.d. - 2.0	n.d. - 8.7	n.d. - 16	n.d. - 1.5	n.d. - 1.0		Lam et al. (2016)
	1.0–15	0.83–14	0.57–26	0.78–9.5	0.41–5.1	0.81–10	2.4–34	1.3–23	0.45–7.7	0.17–4.9	0.32–5.2	Hong et al. (2013)
	n.d. - 16	n.d. - 8.7	0.35–47				n.d. - 110	0.54–31	0.20–5.9	0.20–9.3	0.22–1.3	Naile et al. (2013)
			2.24 -651					0.9–62				Rostkowski et al. (2006)
Norway		n.d. - 0.1	0.0–0.2	0.0–0.1	0.3–0.4	0.0–0.1		0.0–0.1				Kwok et al. (2013)
USA			2.5–2.8					2.6–3.7				Konwick et al. (2008)

* Estimated from Author figures.

and the inherent variability of flows in south eastern Australian rivers. During 2012–13, for instance, rainfall across the Melbourne region was generally below-average, which translated into a reduction of runoff into most of Melbourne's surface waters, including the Werribee River, but not the Yarra River, which had higher than average flow during the sampling period (BOM, 2019). Assuming the data obtained in this pilot study was representative of PFAS concentrations in the sampled waters in 2012–13, then at least 11 kg Σ PFAS entered PPB via the Yarra River and 1 kg Σ PFAS from the Werribee River. The PFAS flux estimated in this study is of the same order of magnitude estimated by Ahrens et al. (2015) in Sweden, but at least a thousand times lower than the amount of PFAS estimated to enter German rivers by Möller et al. (2010).

3.4. Ecological risk of observed PFAS concentrations

The current ANZECC & ARMCANZ 2000 do not provide trigger values for any PFAS. The Guidelines are currently being revised, with the development of draft standards for PFOS and PFOA being fast-tracked (EPA Victoria, 2017). The default value used in Australia is the 95% species protection value, which is designed to allow for 95% species protection in “slightly-moderately disturbed ecosystems.” This description would apply to Site G. The level of PFOS observed at this site (0.0065 $\mu\text{g/L}$) is two orders of magnitude lower than the draft Australian guideline level for total PFOS (0.13 $\mu\text{g/L}$). The highest level of PFOS observed at a freshwater was 0.045 $\mu\text{g/L}$ at site E (Table 1); this concentration is approximately half the draft 95% species protection level for total PFOS. Site E also returned the highest level of PFOA in the study (0.014 $\mu\text{g/L}$), some four orders of magnitude lower than the draft Australian trigger value for total PFOA (220 $\mu\text{g/L}$). The risk quotients (RQ_{med} and RQ_{max}) did not exceed 1 for any residue at either site. When the toxic unit ($\log_{10}\text{TU}$; Liess and Von Der Ohe, 2005) was calculated no chemical had a $\log_{10}\text{TU}_f > -3$; further suggesting that observed PFAS would not have posed a short-term risk to organisms in the freshwaters studied at the time of sampling.

No Australian marine water quality trigger values have as yet been proposed. The European environment quality standards (EQS) adopted in EU Directive 2013/39/EU (EU, 2013) provides for a maximum allowable concentration of PFOS in ‘other surface waters,’ which would seem to include estuaries and coastal waters of the type sampled in this pilot program. None of the estuarine samples would have exceeded the EU ‘other waters’ guideline level (7.2 $\mu\text{g/L}$). Moreover, none of the PFAS observed at estuary sites had RQ above 1 or $\log_{10}\text{TU}$ above -3.

The toxic effects of mixtures can occur at much lower concentrations than observed for individual chemicals (Baas et al., 2009). In that context, six PFASs (PFBS, PFHxS, PFO, PFDA, FOSA, and N-EtFOSAA) were observed in one or more water sample; these PFASs will have similar modes of action, yet when the sum of toxic units ($\Sigma\log_{10}\text{TU}$) was calculated, no sites had $\log_{10}\text{TU}_f$ or $\log_{10}\text{TU}_{\text{alg}}$ above -3 (the level suggested by Liess and Von Der Ohe (2005) as being problematic). When this process was completed for the PFCAs, no water sample had $\log_{10}\text{TU}$ above -3, further suggesting little or no short-term risk to organisms in the estuary waters studied at the time of sampling.

4. Conclusions

The main aim of this reconnaissance was to examine the occurrence of common PFAS in water samples collected from seven creeks and estuaries in the Port Phillip Bay catchment, Victoria, and to assess the risk to aquatic organisms therein by comparing observed concentrations with regulatory guideline values. Eighteen of the 19 screened PFAS were observed on one or more occasion in one or more samples. The detection of common perfluoroalkyl sulphonates such as PFBS (up to 7.0 ng/L), PFHxS (up to 42 ng/L), and PFOS (up to 75 ng/L), as well as perfluoroalkyl carboxylates such as PFBA (up to 11 ng/L, respectively),

PFOA (up to 8.5 ng/L) and PFNA (up to 6 ng/L) in these Victorian estuaries proves that the existence of these PFAS in the Port Phillip environment is potentially of concern in Australia. The lack of exceedances of the draft Australian guideline values for PFOS and PFOA in the freshwater water samples would in and of themselves likely not ‘trigger’ a management response, however further investigation of the potential aquatic ecosystem impact of PFAS in metropolitan Melbourne's urban waters is still warranted.

Declarations

Author contribution statement

Mayumi Allinson: Conceived and designed the experiments; Performed the experiments.

Nobuyoshi Yamashita: Conceived and designed the experiments; Contributed reagents, materials, analysis tools or data.

Sachi Taniyasu, Eriko Yamazaki: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Graeme Allinson: Analyzed and interpreted the data; Wrote the paper.

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Competing interest statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

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